

16. (Amended) A silicon single crystal wafer, which is doped with nitrogen, has an interstitial oxygen concentration of 5 ppma or less, in which at least void type defects and dislocation clusters are eliminated from the entire plane, and the main surface of the silicon single crystal wafer is subjected to an EG treatment.

25. (Amended) A method for producing a silicon single crystal wafer, wherein the wafer is produced from a single crystal pulled under such conditions that the crystal should have an N-region for the entire plane and interstitial oxygen concentration should become 5-8 ppma when the crystal is grown by the Czochralski method with nitrogen doping.

REMARKS

Claims 13-33 are pending. Claims 13-16 and 25 are amended to more particularly point out and distinctly claim the invention. Support for these amendments can be found in the application as filed, for example, at page 14. No new matter is added.

The attached Appendix includes marked-up copies of each rewritten claim (37 C.F.R. §1.121(c)(1)(ii)).

Rejection under 35 U.S.C. §103(a)

The Office Action rejects claims 13-33 under 35 U.S.C. §103(a) as unpatentable for obviousness over Tamatsuka et al. (U.S. 6,162,708) in view of Iida et al. (ELECTROCHEMICAL SOC'Y PROC., Vol. 99-1, pp. 499-510). Applicants respectfully traverse this rejection.

Claims 13, 14, 25 and their dependent claims

The Office Action asserts that the sole difference between Tamatsuka and the invention of independent claims 13, 14, 25 and their dependent claims is the F/G. Applicants disagree with this characterization.

Tamatsuka describes the silicon single crystal wafer of its invention as doped with nitrogen and having an epitaxial layer formed in the surface layer portion of the silicon single crystal wafer. See, Tamatsuka, claim 1. Tamatsuka does not relate to a wafer having an N-region for the entire plane, as in present claims 13 and 25. In addition, Tamatsuka neither

discloses nor suggests the oxygen concentration range of the invention of claims 13, 14 and 25. Since Tamatsuka does not define the oxygen concentration as specifically being 8 ppma or less, an OSF ring generated by nitrogen doping can not be defused.

Tamatsuka describes as its invention that an epitaxial layer is formed in the surface layer portion of a silicon single crystal wafer that is doped with nitrogen. Unlike the invention of claims 13 and 25, Tamatsuka does not relate to a wafer having an N-region for the entire plane. Tamatsuka does not teach such a limitation, and thus cannot have rendered obvious this feature of the claims.

Furthermore, the oxygen concentration disclosed in Tamatsuka is 18 ppma or less. This oxygen concentration range is defined very broadly, and is not defined as the specific, extremely low oxygen concentration of 5-8 ppma as in claims 13, 14 and 25. In particular, the examples of Tamatsuka describe oxygen concentrations of 16 ppma (example 1), 10.5-17.5 ppma (example 2), 10-18 ppma (example 3), and 16 ppma (example 4), all outside of the range claimed in the instant claims. Nowhere does Tamatsuka teach or suggest having the oxygen concentration in the specific, narrower range of claims 13, 14 and 25. Tamatsuka does not teach or suggest that any benefits could be obtained by lowering the oxygen concentration to within the claimed range.

In order to define the oxygen concentration range as in the invention of claims 13, 14 and 25, it is necessary to recognize that OSFs are not generated by utilizing an OSF region expanded by nitrogen doping while the oxygen concentration is 5-8 ppma, and a defect-free wafer can be made from a crystal containing no dislocation loops originating from OSF nuclei. Moreover, since fine oxide precipitates exist in the claimed silicon wafer, the wafer has IG ability. That is, since a silicon single crystal wafer that is doped with nitrogen, has an N-region for the entire plane and an interstitial oxygen concentration of 5-8 ppma is used, a silicon single crystal wafer that is defect-free and has appropriate gettering ability (i.e., a defect-free wafer with IG ability) can be provided.

The instant application recognizes and teaches the use of a specific, narrower range of oxygen concentration, a range not taught or suggested by the cited references. The invention of claims 13, 14 and 25 recognizes that OSFs are not generated by utilizing an OSF region expanded by nitrogen doping while the oxygen concentration is 5-8 ppma, and that a defect-free wafer can be made from a silicon single crystal that contains no dislocation loops originating from OSF nuclei. Since fine oxide precipitates exist in the silicon wafer, the wafer has IG ability. As a result, the silicon single crystal wafer, doped with nitrogen, has an N-region for the entire plane and an interstitial oxygen concentration of 5-8 ppma. Thus, a silicon single crystal wafer that is defect-free and has appropriate gettering ability (IG ability) can be obtained.

Tamatsuka, therefore, does not teach or suggest the invention of claims 13, 14 and 25. Combining Tamatsuka with Iida does not cure the defects of Tamatsuka.

Iida discloses a silicon wafer that is doped with nitrogen and has an N-region for the entire plane. However, the silicon wafer disclosed in Iida does not have an interstitial oxygen concentration of 5-8 ppma. Unlike claims 13, 14 and 25, Iida can not obtain a defect-free wafer with IG ability.

In particular, Iida discloses a silicon wafer that is doped with nitrogen, has an N-region for the entire plane and an interstitial oxygen concentration of 6.4-4.8 ppma. However the oxygen concentration of Iida is represented by ASTM '79 as described on page 500 of Iida. The oxygen concentration defined in the claimed invention is represented by JEIDA as described at, for example, page 19, lines 9-11. The relation between JEIDA and ASTM is $JEIDA \times 1.6 \approx ASTM$ '79. See Shimura, Semiconductor Silicon Crystal Technology, p. 233 (attached). Therefore, the oxygen concentration of 6.4-4.8 ppma (ASTA '79) described in Iida is 4.0~3.0 ppma by JEIDA, which is below the concentration range specified in claims 13, 14 and 25. Thus, Iida does not disclose a wafer having the oxygen concentration of 5-8 ppma (JEIDA) as in claims 13, 14 and 25, and does not teach or

suggest increasing the oxygen concentration to be in the range of 5-8 ppma, as claimed. Iida neither describes nor suggests a defect-free wafer with IG ability.

Even if Tamatsuka is combined with Iida, the combination does not teach or suggest that a silicon wafer that is doped with nitrogen, has an N-region for the entire plane and the interstitial oxygen concentration of 5-8 ppma will provide a wafer that is defect-free and has IG ability. The cited references do not describe the oxygen concentration of 5-8 ppma. In fact, any combination of the references would provide a wafer having an oxygen concentration either well above the claimed range, consistent with the examples of Tamatsuka, or well below the claimed range, consistent with the requirements of Iida. Moreover, neither cited reference teaches or suggests attempting to obtain a defect-free wafer that has IG ability.

Accordingly, one of ordinary skill in the art would not have derived the invention of independent claims 13, 14 and 25, or likewise their dependent claims, from the combination of the cited references.

Claims 15, 16 and their dependent claims

Similarly, the Office Action asserts that the sole difference between Tamatsuka and the invention of independent claims 15, 16 and their dependent claims is the F/G. Applicants disagree with this characterization.

In order to define the oxygen concentration range as in claims 15 and 16, it is necessary to recognize that when an oxygen concentration of 5 ppma or less is used, the wafer shows extremely good defect and electric characteristics. But because it does not contain bulk defects, it lacks gettering ability (IG ability). Therefore, an EG treatment may be performed to impart gettering ability.

A silicon single crystal wafer that simultaneously is defect-free and possesses gettering ability (EG ability) can be obtained for the first time in the claimed invention by the silicon single crystal wafer that is doped with nitrogen, has an N-region for the entire plane

and an interstitial oxygen concentration of 5 ppma or less, and is subjected to an EG treatment. Such a wafer is not disclosed by Tamatsuka.

For at least these reasons and the reasons discussed above with respect to claims 13, 14 and 25, Tamatsuka does not teach or suggest the invention of independent claims 15 and 16. Tamatsuka does not teach or suggest limiting the oxygen concentration to 5 ppma or less, as claimed. Nor does Tamatsuka teach or suggest that the N-region should be for the entire plane, as claimed. Combining Tamatsuka with Iida does not cure the defects of Tamatsuka.

Iida discloses a silicon wafer that is doped with nitrogen and has an N-region for the entire plane. But unlike the invention of claims 15 and 16, Iida can not obtain a defect-free wafer with either IG ability or EG ability.

As discussed above, Iida discloses a silicon wafer which is doped with nitrogen, has an N-region for the entire plane and an interstitial oxygen concentration of 6.4-4.8 ppma by ASTA '79 (but 4.0~3.0 ppma by JEIDA). Thus, the Iida wafer has an oxygen concentration of less than 5 ppma but is not subjected to an EG treatment. Accordingly, the Iida wafer does not have the gettering ability (EG ability) of claims 15 and 16. Iida neither describes nor suggests a defect-free wafer with gettering ability.

Even if Tamatsuka is combined with Iida, the combination does not teach or suggest that a silicon wafer that is doped with nitrogen, has an N-region for the entire plane and the interstitial oxygen concentration of 5 ppma or less and is subjected to an EG treatment will provide a wafer that is defect-free and has EG ability. Although Iida describes the oxygen concentration of 5 ppma or less, Iida does not combine this oxygen concentration with an EG treatment. Moreover, neither cited reference teaches or suggests attempting to obtain a defect-free wafer that has EG ability. Accordingly, one of ordinary skill in the art would not have derived the invention of claims 15 and 16 from the combination of the cited references.

For at least these reasons, the invention of claims 15 and 16, and by the same reasoning their dependent claims, would not have been obvious over Tamatsuka in view of Iida.

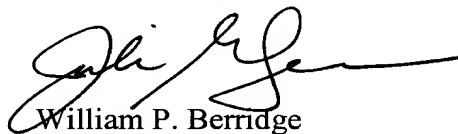
Accordingly, Applicants respectfully request reconsideration and withdrawal of the rejections under 35 U.S.C. §103(a).

Conclusion

In view of the foregoing amendments and remarks, Applicants submit that this application is in condition for allowance. Favorable reconsideration and prompt allowance of claims 13 - 33 are earnestly solicited.

Should the Examiner believe that anything further would be desirable in order to place this application in better condition for allowance, the Examiner is invited to contact Applicants' undersigned representative at the telephone number set forth below.

Respectfully submitted,



William P. Berridge
Registration No. 30,024

Julie M. Seaman
Registration No. 51,156

WPB:JMS/jam

Attachments:

Appendix

"Semiconductor Silicon Crystal Technology," Academic Press, Inc., pp. 226-235.

Date: April 28, 2003

OLIFF & BERRIDGE, PLC
P.O. Box 19928
Alexandria, Virginia 22320
Telephone: (703) 836-6400

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APPENDIX

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Changes to Claims:

The following is a marked-up version of the amended claims:

13. (Amended) A silicon single crystal wafer grown by the Czochralski method, which is doped with nitrogen, and has an N-region for the entire plane and an interstitial oxygen concentration of ~~8 ppma or less~~ 5-8 ppma.
14. (Amended) A silicon single crystal wafer grown by the Czochralski method, which is doped with nitrogen, and has an interstitial oxygen concentration of 5-8 ppma ~~8 ppma or less~~, and in which at least void type defects and dislocation clusters are eliminated from the entire plane.
15. (Amended) ~~The~~ A silicon single crystal wafer ~~according to Claim 13,~~ wherein the, which is doped with nitrogen, has an N-region for the entire plane, and has an interstitial oxygen concentration is of 5 ppma or less, and one main surface of the silicon single crystal wafer is subjected to an EG treatment.
16. (Amended) ~~The~~ A silicon single crystal wafer ~~according to Claim 14,~~ wherein the, which is doped with nitrogen, has an interstitial oxygen concentration is of 5 ppma or less, in which at least void type defects and dislocation clusters are eliminated from the entire plane, and the main surface of the silicon single crystal wafer is subjected to an EG treatment.
25. (Amended) A method for producing a silicon single crystal wafer, wherein the wafer is produced from a single crystal pulled under such conditions that the crystal should have an N-region for the entire plane and interstitial oxygen concentration should become 5-8 ppma ~~8 ppma or less~~ when the crystal is grown by the Czochralski method with nitrogen doping.

Semiconductor Silicon Crystal Technology

Fumio Shimura

*Department of Materials Science and Engineering
North Carolina State University
Raleigh, North Carolina*

*Leave the beaten track occasionally
and dive into the woods. You will be
certain to find something that you
have never seen before.*

Alexander Graham Bell



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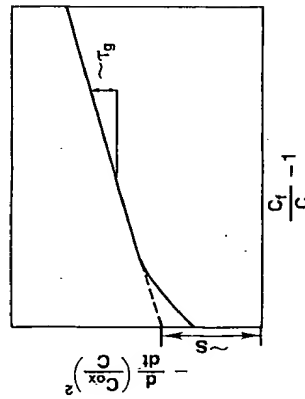


Fig. 6.9. Zerbst plot.

6.2 Chemical Characterization

6.2.1 Impurities in Silicon

The chemical properties that are of most exclusive concern are related to adventitiously induced impurities in processed silicon wafers as well as impurities incorporated into the starting silicon. Many of the impurities tend to be introduced at high temperatures where solubilities are high. On cooling or heat treatment at lower temperatures, precipitation occurs because of decreased solubility. It is very important, as already discussed repeatedly, to characterize silicon wafers by measuring impurity precipitation as well as the concentration. Numerous kinds of diagnostic techniques have been utilized for the measurement of impurities in silicon.¹⁻³ In this section, some techniques that are most commonly used and most useful for silicon characterization are demonstrated.

6.2.2 Radioactivation Analysis

Principle and Characteristics Radioactivation analysis³⁴ is a method considered for the analysis of trace impurities in semiconductor materials in which impurity concentrations in the parts per million to parts per billion range are becoming more and more important. If an analytical sample is exposed to the effect of neutrons or electrically charged particles of suitable energy, nuclear reactions occur in atoms. The products are usually radioactive and the amount is related to the amount of the desired element present in the sample. Activation analysis thus consists of two major processes: (1) the production of a radioactive nuclide from the desired element by some nuclear reaction, and (2) the measurement of the amount of the product. Typically, a relative method is taken for the analysis. This involves activating a standard containing a known amount of the element m_s , as well as the sample containing an unknown amount of the element m_x . The fundamental

relation between the activities formed by activation of the given element in the sample and in the standard, A_x and A_s , respectively, is given by

$$A_x/A_s = m_x/m_s \quad (6.22)$$

The activity A of nuclide i is commonly given by

$$A_i = \Phi \sigma_i N_i [1 - \exp(-\lambda_i t)] \quad (6.23)$$

where Φ is the irradiation particle flux, σ_i the cross section for the reaction producing the nuclide i , N_i the number of target nuclei in the sample available for the reaction producing the nuclide i , λ_i the decay constant for the nuclide i , and t the duration of the irradiation.³⁴ In the course of activation, nuclides are formed not only from the element to be determined but also from most of the other elements present in the sample to be analyzed. The main problem is thus to distinguish radiation of the given nuclide from that of other nuclides. This differentiation can be carried out by either chemical or physical means or by some combination of the two.

Irradiation Sources The choice of an irradiation source implies the choice of the nuclear reaction for producing the desired nuclide. The irradiation sources most commonly used for the analysis of trace impurities in silicon are neutrons and charged particles. Neutrons produced by nuclear reactions have in common the ability to be thermalized, in which energy state they have large probabilities for capture by most elements to form measurable radioactive nuclides as a result of the (n, γ) nuclear reaction. On the other hand, charged particles are very useful for light elements that do not yield convenient neutron reactions or that require neutron energies not attainable in nuclear reactions or neutron generators.

Neutron Activation Analysis Neutron activation analysis (NAA) meets most of the requirements for the study of trace impurities in silicon.^{35,36} Gamma-ray (γ -ray) spectroscopy, in which the (n, γ) reaction is used, has a very high sensitivity for most elements of the periodic table beyond neon. Exceptions are light elements (i.e., B, P, and S) and heavy elements (i.e., Tl, Pb, and Bi) that do not become γ -ray emitters but only beta (β) emitters. Therefore, the analysis of P, one of the common dopants in silicon, has been performed with β -ray spectroscopy. As for B, another common dopant in silicon, the charged-particle activation analysis (CPAA) discussed next has been used. By means of NAA, a systematic survey on the transition-metal group impurities, which reside in starting silicon and are introduced during the device manufacturing processes, has been conducted by Schmidt and Pearce.³⁷

Table 6.2 Detection Limits for CPAA^a

Detection limit	Elements
< 1 ppba	B, ^b C, ^b N, ^b O, ^b Ca, Y, Pr, Gd
1–10 ppba	Li, Ti, Cr, Co, Ni, Cu, Zn, Ga, Ge, Br, Rb, Zr, Ru, Cd, Sn, Te, Ba, Hf, Os, Ir, Pt, Tl, Pb, Bi, La, Ce, Eu, Ho, Er, Yb, Lu
10–100 ppba	H, He, Na, Mg, Al, Si, P, S, V, Fe, As, Se, Sr, Nb, Rh, Pd, Ag, Sb, Cs, Au, Hg
0.1–1 ppm	Cl, Mn, In, Re
1–10 ppm	K, Ta

^a After Nakajima and Kohara.⁴⁰^b The detection limits for these elements in silicon have been reported as: B, 10 ppba³⁴; C, 20 ppba⁴¹; N, 2 ppba⁴²; and O, 10 ppba.⁴²

Charged-Particle Activation Analysis Charged-particle activation analysis (CPAA) is well suited to determining light elements (e.g., B, C, O, N) at the parts per billion level in silicon.^{38,39} The particles used in CPAA include protons (¹H⁺), deuterons (²H⁺), tritons (³H⁺), helium-3 ions (³He⁺), and helium-4 ions or alpha particles. (⁴He⁺ or α). A major feature of CPAA is that different nuclides can be obtained from a given target isotope, depending on the nature and energy of the irradiating particle. The nuclear reactions commonly adopted for the analysis of B, C, N, and O are ¹¹B(p, n)¹¹C, ¹²C(³He, ⁴He)¹¹C, ¹⁴N(p, ⁴He)¹¹C, and (³He, p)¹⁸F, respectively.^{38,40}

Although the major thrust of CPAA remains in the field of light-element analysis, highly sensitive CPAA procedures have been devised for most stable elements. The detection limits reported for 72 elements are given in Table 6.2.^{40–42}

6.2.3 Infrared Spectroscopy

Principle and Characteristics Atoms or atomic groups in molecules are in continuous motion with respect to each other. The possible vibrational modes in a polyatomic molecule, acetaldehyde for example, can be visualized from mechanical models of the system as illustrated in Fig. 6.10.⁴³ Atomic masses and bonding forces of the chemical links are represented by balls and by springs that connect and keep the balls in positions of balance. Their motion can be regarded as being composed of two components, the stretching and bending vibrations. If the vibrating mode is observed with a stroboscopic light of variable frequency, certain light frequencies will find the balls appear to remain stationary. These represent the specific vibrational frequencies.⁴³ The frequencies depend not only on the nature of the particular bonds themselves, but also on the entire molecule and its environment.

As shown in Fig. 3.13, the infrared (IR) covers the region from 0.7 to 500 μm in wavelengths or from 14,000 to 20 cm^{-1} in wave numbers. The

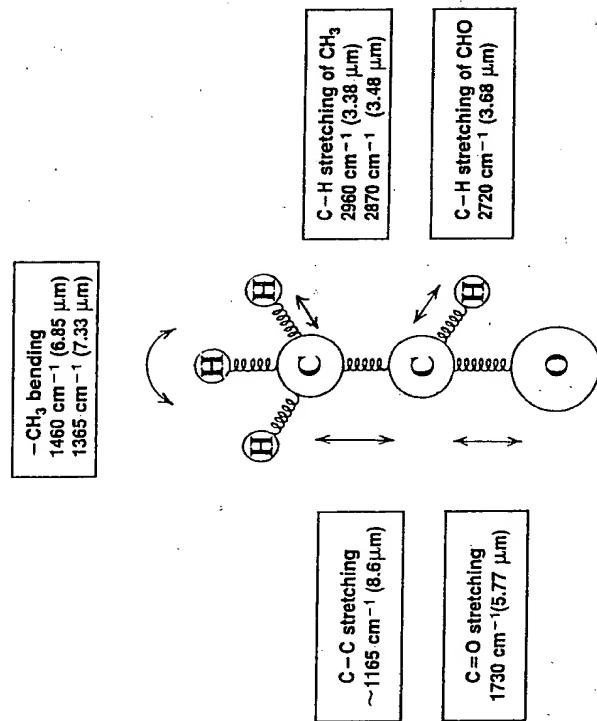


Fig. 6.10. Vibrational models and characteristic frequencies of acetaldehyde. (After Willard *et al.*⁴³ Reproduced with the permission of Wadsworth Publishing Company.)

range of special interest is between 400 and 2000 cm^{-1} , which covers almost all absorption due to impurities of interest in silicon. When the sample is irradiated by an IR beam whose frequency is changed continuously, the molecule will absorb certain frequencies as the energy is consumed in stretching or bending different bonds. The transmitted beam corresponding to the region of absorption will naturally be weakened, and thus recording of the intensity of the transmitted beam versus wave numbers or wavelength will give spectra that show characteristic absorption bands. The absorption bands are a direct reflection of the state of molecular bonds, and thus this aspect leads to the qualitative analysis. Moreover, the absorption intensity is proportional to the amount of the specific element present in the sample, and this leads to quantitative analysis by converting into concentration using the calibration curve obtained with another direct measuring technique such as CPAA. Infrared spectroscopy has been used for the analysis of various impurities such as dopants,⁴⁴ oxygen, carbon, and nitrogen in silicon. The great advantage of IR spectroscopy is that both qualitative and quantitative analyses can be performed nondestructively, quickly, and less expensively. Analytical sensitivity strongly depends on sample thickness. For silicon, routine analyses can be performed for common silicon wafers of several hundred micrometers to 1 mm in thickness; however, thicker samples (e.g., 2–10 mm) are recommended for precise analyses. Moreover, IR spectroscopic

Table 6.3 Detection Limits of Impurities for IR Spectrophotometry at ~ 10 K and 300 K^a

Element	Limits (atoms/cm ³)	
	~ 10 K	300 K
Oxygen	3×10^{13}	2.5×10^{15}
Carbon	—	5×10^{15}
Nitrogen	—	2×10^{15}
Boron	3.1×10^{11}	—
Aluminum	2.1×10^{12}	—
Gallium	2.7×10^{12}	—
Indium	1.6×10^{13}	—
Phosphorus	1.5×10^{11}	—
Arsenic	2.7×10^{11}	—
Antimony	3.1×10^{11}	—

^a After Keenan and Larabee,⁶ Pajot,⁴⁵ ASTM,⁴⁶ and Ito *et al.*⁴⁷

analysis at low temperatures results in higher sensitivity for impurities in a sample, since the ionized carriers in silicon begin to "freeze out"—that is, the absorption due to the free carriers becomes negligibly small—at low temperatures.⁴⁴ Table 6.3 lists the detection limits of impurities in silicon for IR spectroscopy at ~ 10 K and 300 K.^{6,45-47} It should be noted that IR spectroscopy cannot be used for heavily doped ($> 5 \times 10^{17}$ atoms/cm³ or $< 0.1 \Omega \text{ cm}$) n^+ and p^+ silicon substrates due to free carrier absorption interferences,⁴⁸ unless the sample is irradiated with electrons that trap the free carriers.⁴⁹

Spectrophotometers Most IR spectrophotometers are double-beam instruments in which two equivalent beams of radiant energy are taken from the source.⁴³ The source beam strikes alternately the reference and sample paths by means of a combined rotating mirror and light interrupter. In order to disperse the radiation and focus successive wavelengths on a detector, a conventional spectrophotometer uses a prism or grating.

An alternative spectrophotometer is a Fourier-transform IR (FTIR) spectrophotometer,^{6,43} which has been widely used in the silicon industry. An FTIR spectrophotometer basically consists of two parts: (1) an optical system that uses an interferometer, and (2) a dedicated computer that controls optical components, collects and stores data, performs computations on data, and displays spectra. Although some negative aspects of FTIR spectroscopy have been pointed out,⁵⁰ FTIR generally offers potential advantages compared with conventional dispersion IR spectroscopy: (1)

higher signal-to-noise (SN) ratios for spectra obtained under conditions of equal measurement time, and (2) higher accuracy for spectra taken over a wide range of frequencies. The most important advantage of FTIR spectrophotometer results from the use of an interferometer instead of a prism or grating, which requires energy-wasting slits. As regards the detection limit and accuracy of impurity analysis, at least for oxygen in silicon, no essential difference has been found between a dispersive-type IR and an FTIR spectrophotometer.⁵¹

Oxygen Analysis Since oxygen was identified by IR absorption in CZ silicon crystals in 1956,⁵² IR spectroscopy has been a routine technique to determine the oxygen concentration in silicon crystals.⁴⁵ Moreover, IR spectroscopy has been commonly used for the characterization of oxygen precipitation in silicon crystals.⁵³⁻⁵⁶ An interstitial oxygen atom that bonds with two adjacent silicon atoms (Fig. 5.35) gives rise to three basic vibration modes, as shown in Fig. 6.11.^{52,57} With Si-O distances of 1.6 Å and assuming the Si-Si distance to be essentially unchanged (2.34 Å), the bond angle Si-O-Si will be approximately 100° for a hypothetical nonlinear Si₂O molecule.⁵² The characteristic frequencies of the three basic absorptions ν_{01} , ν_{02} , and ν_{03} at room temperature are 1205 cm⁻¹, 515 cm⁻¹, and 1106 cm⁻¹, respectively.⁵⁷ Figure 6.12a shows IR absorption spectra obtained at room temperature for as-grown CZ silicon that is commercially available.⁵⁸ Absorption peaks due to interstitial oxygen are clearly observed at 515 cm⁻¹ (ν_{02}) and 1106 cm⁻¹ (ν_{03}); however, ν_{01} absorption is too weak to be

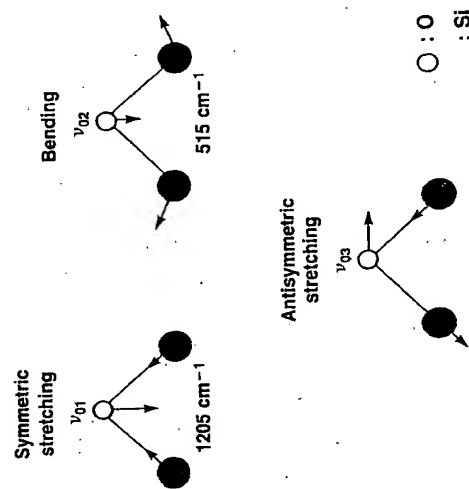


Fig. 6.11. Three basic vibrational modes of interstitial oxygen in silicon. (After Hrostowski and Kaiser.⁵⁷)

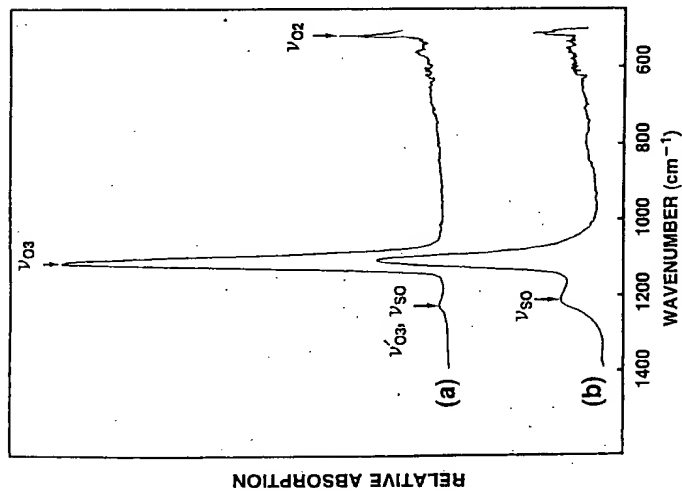


Fig. 6.12. Infrared absorption spectra for CZ silicon wafer: (a) as grown and (b) after heat treatment at 1000°C for 64 h. (After Shimura *et al.*⁵⁸)

observed at room temperature. The relative intensity of ν_{O_2} and absorption to that of ν_{O_3} is about 0.25. As for the weak absorption observed around 1225 cm^{-1} , it has been attributed to grown-in SiO_2 precipitates, (i.e., ν_{SO}),⁵⁴ which have absorption at 1224 cm^{-1} ,⁵³ and/or to the ν_{O_3} subpeak, which is expected at 1227 cm^{-1} .⁵⁹

As mentioned briefly in the footnote on page 178, interstitial oxygen concentration $[\text{O}_i]$ is calculated using the absorption coefficient of ν_{O_3} at 1106 cm^{-1} (i.e., $\lambda = 9.04 \mu\text{m}$) as follows:

$$[\text{O}_i] = f_c \alpha_{O_3} \quad (\times 10^{17} \text{ atoms/cm}^3) \\ = 2f_c \alpha_{O_3} \quad (\text{ppma}) \quad (6.24)$$

where f_c is the conversion factor and α_{O_3} is given by

$$\alpha_{O_3} = \ln(I_0/I)/x \quad (6.25)$$

where I is transmitted intensity at the absorption peak, I_0 the baseline intensity, and x the specimen thickness (cm). The detailed procedure for $[\text{O}_i]$ measurement is given in Ref. 46. The trouble here is that three different

conversion factors are in common use in the silicon industry today for obtaining $[\text{O}_i]$ by IR absorption measurement at room temperature. The factor $f_c = 2.45$ is commonly referred to as "DIN"⁶⁰ or "New ASTM,"⁴⁶ while $f_c = 4.81$ is "Old ASTM."⁶¹ In addition, $f_c = 3.03$, which is commonly referred to as "JEIDA,"⁵¹ has been recently reported. Because of the diversity of these values, it is necessary to identify the conversion factor used when $[\text{O}_i]$ in silicon is discussed. In this book, the conversion factor $f_c = 2.45$ is used. However, it should be noted that JEIDA value ($f_c = 3.03$) is expected to be universally accepted in the near future.⁶² Heat treatment leads to the precipitation of supersaturated interstitial oxygen in CZ silicon. For example, Fig. 6.12b shows the IR absorption spectra of CZ silicon subjected to a heat treatment at 1000°C for 64 hr.⁵⁸ Comparing the IR spectra for the as-grown sample shown in Fig. 6.12a, one clearly observes that the absorption ν_{O_3} due to interstitial oxygen decreases, and inversely the absorption ν_{SO} due to oxygen precipitates (SiO_2) increases. If the initial interstitial oxygen concentration is denoted as $[\text{O}_i]_0$ and the concentration after a heat treatment as $[\text{O}_i]_t$, the precipitated oxygen concentration $\Delta[\text{O}_i]$ is simply given as the difference:

$$\Delta[\text{O}_i] = [\text{O}_i]_0 - [\text{O}_i]_t$$

The size of measurement area, namely an IR beam size, depends on the respective spectrometer. Typical sizes are 5 mm (width) \times 15 mm (height) and 15 mm in diameter for the most commercial IR spectrometers.⁵¹ In order to obtain the microprofiles of oxygen concentration or oxygen precipitation, a scanning IR absorption technique using a collimated laser beam, for example, a double-heterostructure $\text{PbTe/Pb}_{0.82}\text{Sn}_{1.18}\text{Te}$ laser ($\lambda = 9.04 \mu\text{m}$, spatial resolution $\approx 200 \mu\text{m}$ diameter),⁶³ and a CO_2 laser ($\lambda = 9.17 \mu\text{m}$, spatial resolution $\approx 30 \mu\text{m}$ diameter)⁶⁴ has been developed. By applying this technique, oxygen striations in CZ silicon crystals have been observed and correlated with thermally induced microdefects.⁶⁵

It should be noted that the absorption ν_{O_3} involves only interstitial oxygen, but not all oxygen, although almost all oxygen atoms occupy interstitial sites in silicon.⁶⁶ CPAA, instead of IR spectroscopy, is adequate for the measurement of the absolute concentration of oxygen in silicon.

Carbon Analysis Substitutional carbon in silicon gives rise to the IR absorption at 607 cm^{-1} , ν_c , and this peak has been used for the determination of carbon concentration $[\text{C}_i]$ in silicon crystals.⁶⁷ As shown in Fig. 6.12a, the absorption due to carbon is usually not observed in common CZ silicon crystals, which in turn implies that the concentration of carbon in common CZ silicon is less than 5×10^{15} atoms/ cm^3 . Figure 6.13 shows the IR absorption spectra for a CZ silicon crystal in which carbon is intentionally

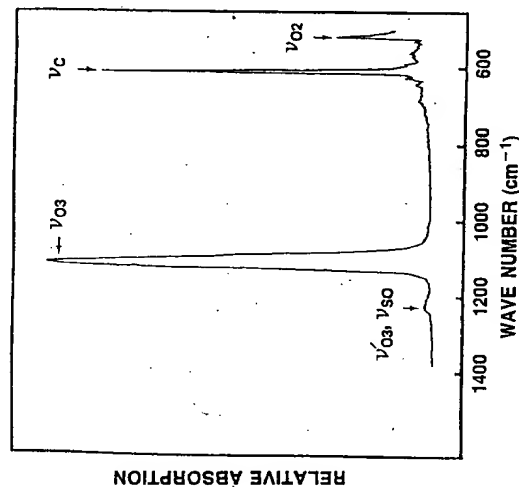


Fig. 6.13. Infrared absorption spectra for as-grown CZ silicon doped with carbon at ~ 6 ppm. (After Shimura *et al.*⁵⁸)

doped.⁵⁸ The concentration of substitutional carbon $[C_s]$ is calculated with the following equation according to the standard procedure given in Ref. 68:

$$\begin{aligned} [C_s] &= \alpha_c \quad (\times 10^{17} \text{ atoms/cm}^3) \\ &= 2\alpha_c \quad (\text{ppma}) \end{aligned} \quad (6.26)$$

where α_c is the absorption coefficient for ν_c at 607 cm^{-1} . In contrast to the conversion factor for interstitial oxygen, the factor of unity has been universally used in the silicon industry since 1965. However, detailed analyses have recently been performed for the concentration of carbon in silicon by means of both IR and CPAA techniques, and the following equation has been proposed⁶⁹:

$$[C_s] = (0.85 \pm 0.09)\alpha_c \times 10^{17} \text{ atoms/cm}^3 \quad (6.27)$$

A detailed examination of the calibration of carbon concentration is required in order to meet an increasing interest in carbon in silicon crystals. Again, it should be noted that the absorption ν_c involves only substitutional carbon, but not all carbon, in silicon.

6.2.4 Secondary Ion Mass Spectroscopy

Principle and Characteristics When an energetic primary ion beam with an energy typically between 5 keV and 15 keV impinges on the surface of a sample, the material is sputtered off in the form of atoms and ions, and ejected

from the surface. A small fraction of these atoms is ionized either positively or negatively, and the sputtered secondary ions are mass analyzed with a magnetic sector or quadrupole analyzer.⁷⁰ The secondary ion signal can be recorded in four ways^{71,72}: (1) by a value for the ion current of the emitted ion selected, (2) by an image displayed on a fluorescent screen in the form of the distribution of an element on the sample surface, (3) by an image formed on an electron-sensitive photographic film, and (4) by an image on a resistive anode encoder (RAE). The mass analyzed is directly related to species, and the intensity of the detected signal is proportional to the concentration of the element in the sample.

The diameter of an analyzed surface is usually a few hundred micrometers, but information may be obtained from a surface of $1\text{--}25 \mu\text{m}$ in diameter by using a focusing system.⁷³ The sputtering rate for silicon is usually a few angstroms per second, but can be as high as 1000 \AA per second for deep depth profiles. Thus, the secondary ion mass spectroscopy (SIMS), which is alternatively called *ion microprobe mass analysis* (IMMA or IMA), leads to a localized qualitative and quantitative analysis for impurities contained in a small selected volume of the sample surface. This aspect characteristically distinguishes SIMS from the other above-mentioned analytical techniques, which offer the bulk concentrations of impurities in a sample. This technique thus provides in-depth information on atomic constituents by monitoring one or more secondary ion signals with time as the sputtering process removes the surface atoms of a sample. From the electronic device point of view, this depth-profiling aspect has become the most important use of SIMS.⁷⁴

Moreover, SIMS has two major capabilities that make it highly useful for the characterization of semiconductor materials used for electronic device fabrication: (1) it is capable of detecting all the elements including H and He, and (2) it can quantify these elements at parts per million atomic to parts per billion atomic orders. Table 6.4 lists the SIMS bulk detection limits of "order of magnitude" in silicon.⁷⁵ These are the optimum detection limits obtained by state-of-the-art SIMS technology, and apply to bulk measurements. If SIMS is used to profile or image an element, the detection limit is expected to be worse. It should be noted also that the detection limit strongly depends on the SIMS system used, particularly on the species of primary ion beams and sputtering rate, and because of the complexity of SIMS, process standards are required to apply SIMS to a problem requiring quantitative analysis.

Depth Profiling of Impurities For the semiconductor device technology, it is very important to measure impurity distribution, particularly the distribution of dopants, in the device active regions. Moreover, the analysis of the diffusive and reactive processes between metal, dielectric films, and substrates